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## (54) ELECTRODE CATALYST COMPOSITION, ELECTRODE MATERIAL, AND MANUFACTURE THEREOF

(57)Abstract:

**PURPOSE:** To retard drop in water repellency in a catalyst layer, stably maintain a three-phase interface in the catalyst layer for a long period of time, and lengthen the life of the catalyst layer in a fuel cell.

**CONSTITUTION:** An electrode catalyst layer containing conductive powder such as carbon black on which a platinum catalyst is supported, a powdery binding resin having water repellency such as polytetrafluoroethylene(PTFE), and pitch fluoride is formed on a conductive base material.

Pitch fluoride, different from fluoro resin such as PTFE, has low melt viscosity, is soluble in a fluorine base solvent, and has higher water repellency than PTFE. Pitch fluoride can uniformly be permeated and diffused in the catalyst layer by baking the powdery pitch fluoride or impregnating a pitch fluoride solution, and a uniform three-phase interface is formed.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] When this invention forms the catalyst bed of electrodes for fuel cells, such as a phosphoric acid type, it relates to a useful electrode catalyst constituent, the electrode material using this constituent, and its manufacturing method.

[0002]

[Description of the Prior Art] A fuel cell has the advantage that there is very little generating of a public nuisance substance, and there are also few noise emitting sources. Among fuel cells, a phosphoric acid fuel cell provides PORASU negative pole and anode which formed the catalyst bed in the both sides of an electrolysis solution, constitutes a unit cell, and has the structure which laminated each unit cell via the separator. In order to form a gas passageway, the slot is usually formed in said negative pole and the anode by cutting etc.

[0003] In order that said catalyst bed may have big influence on the conversion efficiency to electrical energy, various proposals are made about the catalyst composition. For example, to JP,57-168473,A. The fuel cell electrode which has a mixture layer containing the conductive substance (graphite-grains child) which has the volume more than  $10^5$  double [ of the volume of the grain of maximum size in the conductive ultrafine particle (acetylene black) which supported the platinum catalyst on the conductive base material, and this ultrafine particle ] is indicated. In the gas diffusion electrode which has arranged the hydrophobic layer to the gas side, the gas diffusion electrode of the fuel cell which constituted the hydrophobic layer from mixtures (for example, graphite, activated carbon, etc.) of different carbon powder of the water repellence combined with the fluoro-resin is indicated by JP,61-225768,A.

[0004] The air pole for fuel cells using the porous base material with which it was impregnated and which heat-treated polytetrafluoroethylene at 370-430 \*\* is indicated by JP,59-157963,A. Since the melt viscosity of polytetrafluoroethylene can be reduced in this prior art reference by said heat treatment and it can be made to reveal uniform water repellence, said air pole is indicated to be

useful as an electrode of the fuel cell which uses methanol as liquid fuel. The charge of gas diffusion electrode material which becomes JP,57-30270,A from the porous-structure object containing conductive substance powder, powdered polytetrafluoroethylene, and fibrous polytetrafluoroethylenes, such as carbon black, is indicated.

[0005]The method of forming a catalyst bed on a porosity pole substrate using the mixture containing the powder, the fluoro-resin, and carrier fluid which supported the platinum catalyst is indicated by JP,1-292755,A.

[0006]Thus, a catalyst bed applies the conductive carbon black which supported the platinum catalyst, and the constituent containing powder-like polytetrafluoroethylene, carries out heating calcination, makes polytetrafluoroethylene bind to a porous electrode base, and is usually formed in it. The three-phase zone which comprised a catalyst phase-fuel gas phase-electrolyte phase exists in the catalyst bed of the fuel cell provided with such a catalyst bed. When the catalyst bed containing powder-like fluoro-resins, such as polytetrafluoroethylene, is calcinated, however, since the melt viscosity of a fluoro-resin is high, It is difficult for the catalyst in the fine pores of a catalyst bed, or the surface of conductive carbon black to make a fluoro-resin reach certainly, and the water-repellent part and non-water-repellency part by a powder-like fluoro-resin localize.

Therefore, high water repellence cannot be uniformly given to the catalyst bed which has fine pores and a channel (passage), and uniform and detailed fine pores or channel (passage) cannot raise contacting efficiency of a three phase ingredient.

[0007]And when a fuel cell is operated, the three-phase zone formed of fuel gas, an electrolysis solution, and a platinum catalyst is maintained by the water repellence on polytetrafluoroethylene and the surface of carbon black, and the voltage in constant current density is high at the beginning of power generation. However, the water repellence by polytetrafluoroethylene and the water repellence on the surface of carbon black fall, and electrolysis solutions, such as phosphoric acid, permeate the inside of a catalyst bed deeply as operation time becomes long. Therefore, potential difference will become small, if the touch area and the electrochemical reaction efficiency of the rate of the three-phase zone of a catalyst bed and a three phase ingredient fall and current density is fixed. A catalyst bed may drop out of a conductive base material by a local power surge etc. Therefore, maintaining a three-phase zone, at high efficiency, a long time cannot be covered and a fuel cell cannot be operated stably.

[0008]In order to control osmosis of the electrolysis solution inside a catalyst bed, it is thought useful to increase content of fluoro-resins, such as polytetrafluoroethylene. However, if a catalyst bed is made to contain a water-repellent high fluoro-resin so much, attainment of electrolysis solutions, such as phosphoric acid to a platinum catalyst, will be controlled. Therefore, the rate of a three-phase zone cannot decrease and electrochemical reaction efficiency cannot be raised.

[0009]

[Problem(s) to be Solved by the Invention]Therefore, the purpose of this invention controls a water-repellent fall, and there is in providing the electrode catalyst constituent which continues at

a long period of time and can maintain the three-phase zone in a catalyst bed stably.

[0010]Other purposes of this invention are to provide the electrode catalyst constituent which can extend the life-span of [ the catalyst bed in a fuel cell ].

[0011]When the purpose of further others of this invention covers a long time and operates a fuel cell stably at high efficiency, there is in providing a useful electrode catalyst constituent.

[0012]Other purposes of this invention are to provide an electrode material provided with the catalyst bed which has the outstanding characteristic like the above, and a manufacturing method for the same.

[0013]

[Elements of the Invention]If this invention persons process a catalyst bed in a fluoridation pitch wholeheartedly paying attention to having softening temperature (melting point) as a result of examination while having water repellence with high (1) fluoridation pitch and (2) solid-state fluoridation pitch are solvent fusibility, Even if it operated for a long time, it found out that a water-repellent fall in a catalyst bed can be controlled, and that a three-phase zone was formed uniformly, and this invention was completed.

[0014]That is, an electrode catalyst constituent of this invention contains a catalyst component, a conductive granule, and a fluoridation pitch. Powder-like bending resin in which said constituent has water repellence further. For example, fluoro-resins, such as polytetrafluoroethylene, a tetrafluoroethylene hexafluoropropylene copolymer, and a tetrafluoroethylene perfluoroalkyl vinyl ether copolymer, may be included. a fluoridation pitch -- a solid state particulate matter -- or it may be used as liquefied. There is the special feature of an angle of contact over water being large, and a fluoridation pitch having high water repellence compared with fluoro-resins, such as polytetrafluoroethylene, and being solvent fusibility. Catalyst components, such as a platinum group catalyst, may be supported to conductive granules, such as conductive carbon powder grain.

[0015]An electrode material of this invention which can be used as an electrode of a fuel cell can be manufactured by forming a catalyst bed which contains said constituent in a conductive base material. A catalyst bed may heat-treat.

[0016]In this specification, a "catalyst bed" means a layer formed with a constituent containing a catalyst component, and it distinguishes from catalyst components, such as a platinum catalyst.

[0017]An electrode catalyst constituent is \*\*\*\*\* about a catalyst component, a conductive granule, and a fluoridation pitch. A platinum group catalyst component containing platinum group metals, such as various catalysts for which said catalyst component promotes an oxidation-reduction reaction in a fuel cell, for example, a ruthenium, rhodium, palladium, osmium, iridium, platinum, and these alloys, are contained. these catalyst components -- a kind -- or two or more sorts can be used. As a catalyst component, platinum or a platinum alloy is usually used in many cases.

[0018]As a conductive granule, carbonaceous particulate matters, such as conductive carbon

black, such as a corrosion-resistant and conductive high particulate matter, for example, acetylene black, furnace black, channel black, and Ketchen black, activated carbon, and black lead, etc. are mentioned. these conductive granules -- a kind -- or two or more sorts can be used. Conductive carbon black is used among these conductive granules in many cases. specific surface area of a conductive granule --  $20-4500\text{m}^2/\text{g}$  -- it is a  $30-3000\text{-m}^2/\text{g}$  grade preferably. Although particle diameter of a conductive granule changes greatly with the kinds, 0.01-1 micrometer of particle diameter of carbon black generally used is about 0.02-0.1 micrometer preferably, for example.

[0019]Content of a conductive granule is about 40 to 70 % of the weight still more preferably 30 to 75% of the weight preferably ten to 80% of the weight to the whole constituent, for example.

[0020]As for said catalyst component, in order to raise conversion efficiency to an oxidation-reduction reaction and electrical energy, being supported by conductive granule is preferred. In a conductive granule with which a catalyst component was supported, a conductive granule with which a catalyst component is not supported may be intermingled. A conductive granule which supported a catalyst component can be obtained by making a conventional method, for example, a conductive granule, support a solution of a catalyst component by methods, such as spraying and immersion, or kneading a conductive granule and a solution of a catalyst component, drying, calcinating if needed or presenting a reduction reaction. A holding amount of a catalyst component is about 5 to 20 % of the weight preferably one to 25% of the weight to the total quantity of a catalyst component and a conductive granule, for example.

[0021]And in order to continue at a long period of time and to maintain the water repellence of a porosity catalyst bed, an electrode catalyst constituent of this invention contains a fluoridation pitch. Although a fluoridation pitch may be liquefied, in order to cover a long time and to operate stably, at operating temperature of a fuel cell, a nonvolatile fluid, especially a nonvolatile solid state fluoridation pitch are used for it in many cases. A solid state fluoridation pitch is indicated by JP,62-275190,A. This solid state fluoridation pitch is obtained by fluorinating a pitch with fluorine gas.

[0022]Generally, a pitch has the structure over which a nucleus which has the layer system which an aromatic condensation six membered ring flat surface laminated, and constitutes a six membered ring flat surface constructed the bridge by aliphatic hydrocarbon groups, such as methylene. As a pitch, for example Petroleum bottoms, a naphtha thermal decomposition residue, an ethylene bottom product oil, A pitch which distilled a petroleum system or Carboniferous system heavy oil, such as coal liquid and coal tar, and removed low boiling point components of less than 200 °C of boiling points, a pitch which performed heat treatment, catalytic hydrotreating, etc. to this pitch further, etc. are mentioned. After distilling an isotropic pitch, a mesophase pitch, a hydrogenation mesophase pitch, a petroleum system, or Carboniferous system heavy oil and, removing low boiling point components for example, more specifically, meso carbon micro beads etc. which consist of a generated mesophase sphere are contained in a pitch.

[0023]A solid state fluoridation pitch is obtained by making a pitch and fluoride react at about 0-

350 \*\*, for example. Following methods are more specifically mentioned.

[0024](1) How to carry out the direct reaction of a pitch and the fluorine gas at about 0 - temperature of 350 \*\* of abbreviation. Desirable reaction temperature is the temperature below the softening point of pitch. Although fluoride pressure in particular is not limited, the range of 0.07-1.5 atmospheres is generally used, for example. In this reaction, fluorine gas may be used as it is, and may be diluted and used with inactive gas, such as nitrogen, helium, argon, and neon. [0025]An obtained fluoridation pitch consists of a carbon atom and a fluorine atom substantially, and a F/C atomic ratio is 0.5 to about 1.8, for example. Such a fluoridation pitch shows the characteristic of following (a), (b), (c), and (d).

[0026](a) In (b) X linear-light electronic spectroscopic analysis which shows a peak of maximum strength near  $2\theta = 13^\circ$  in a powder X diffraction, and shows a peak whose intensity is smaller than said peak near  $2\theta = 40^\circ$ , A peak which is equivalent to CF group at 290.0\*\*1.0 eV, and a peak which is equivalent to CF<sub>2</sub> group near 292.5\*\*0.9 eV are shown, In (d) 30 \*\* which can form a film with (c) vacuum deposition whose ratio of strength of a peak equivalent to CF<sub>2</sub> group to a peak equivalent to CF group is 0.15 to about 1.5, an angle of contact over water is 141 degrees \*\*8 degrees.

[0027]It is white thru/or yellowish white, or a brown solid, and said solid state fluoridation pitch is excellent in a water resisting property and chemical resistance, and is a very stable compound.

[0028]A fluoridation pitch can also be obtained with a gestalt of the shape of transparent resin. Such a transparent resin-like fluoridation pitch (2) fluoridation pitch, for example Under fluorine gas atmosphere, Temperature up of the about 0.1-3 \*\*/minute can be preferably carried out to about 250-400 \*\* with a heating rate about [ 0.5-1.5 \*\* ] a part for /, and predetermined time, for example, by making it react preferably for about 6 to 12 hours, can obtain for about 1 to 18 hours. An obtained transparent resin-like fluoridation pitch shows the following characteristics, for example.

[0029](e) light transmittance: in F/C=1.5-1.7 (f) wavelength of 250-900 nm -- not less than 90% (g) average molecular weight: -- 1500-2000 (h) softening-temperature: -- 150-250 \*\* -- a fluoridation pitch of these -- a kind -- or two or more sorts can be used. A fluoridation pitch obtained by a method of the above (1) and a fluoridation pitch of the shape of transparent resin acquired by a method of the above (2) are contained in a desirable fluoridation pitch.

[0030]the solid state fluoridation softening point of pitch or the melting point -- not less than 100 \*\* -- desirable -- 125-400 \*\* -- further -- desirable -- 150-350 -- it is about 200-350 \*\* especially. As for the solid state fluoridation softening point of pitch or the melting point, it is preferred to use a fluoridation pitch which can choose according to operating temperature of a fuel cell, and has softening temperature or the melting point of a fuel cell higher than operating temperature.

[0031]Said fluoridation pitch has corrosion resistance and chemically high heat resistance at inertness, and melt viscosity is small while having softening temperature (melting point). And a fluoridation pitch has the special feature that water repellence is higher than

polytetrafluoroethylene. Therefore, a catalyst bed is made to contain by making a fluoridation pitch into a particulate matter, heating or by carrying out baking treatment, detailed fine pores of a porous catalyst layer and the surface of a conductive granule can be made permeated, spread or impregnated uniformly, and detailed fine pores etc. which were not able to be used conventionally can be used effective in an electrode reaction. While being able to enlarge a usable area of a three-phase zone and contacting efficiency of a three phase ingredient which comprise said catalyst component, a conductive granule, and water-repellent binding resin, high electrolysis solution-proof nature and high water repellence over phosphoric acid etc. can be given to a three-phase zone. Rather than a water-repellent channel (passage) formed of polytetrafluoroethylene, since a water-repellent channel of a still more detailed path can be formed, a minute three-phase zone can be formed and a uniform electrochemical reaction can be performed. Therefore, while continuing at a long period of time, being able to maintain a three-phase-circuit interface stably, and a local power surge's etc. not occurring but being able to extend the life-span of [ a catalyst bed ], a contact rate of a three phase ingredient can be raised and conversion efficiency to electrical energy can be raised.

[0032]When using said solid state fluoridation pitch as a particulate matter, particle diameter of a fluoridation pitch, What is necessary is just a range which does not spoil dispersibility, perviousness, etc. within a catalyst bed, and about 0.01-5-micrometer about 0.01-15 micrometers of mean particle diameter of 20 micrometers or less are about 0.01-3 micrometers still more preferably especially preferably.

[0033]moreover -- heating or the calcination temperature should just be the temperature which a solid state fluoridation pitch can diffusion permeate -- temperature more than the solid state fluoridation softening point of pitch or the melting point -- 200-400 \*\* is about 250-380 \*\* still more preferably preferably.

[0034]An angle of contact [ as opposed to / in / can control the water repellence of said fluoridation pitch with a reaction condition, the degree of fluorination, etc., and / 30 \*\* / water ], In a sessile drop method, not less than (for example, 120 degrees - 150 degrees) 120-degree not less than 110 degrees are about 125-150 degrees still more preferably preferably as opposed to polytetrafluoroethylene being about 105 degrees.

[0035]Unlike polytetrafluoroethylene, said fluoridation pitch has the special feature of being meltable in a fluorine system solvent. Solution viscosity of a fluoridation pitch is also small. Therefore, a solid state fluoridation pitch may be used as dispersion liquid, such as a solution which a solvent was made to dissolve or distribute, or an emulsion. If a fluoridation pitch is used as a solution or dispersion liquid, compared with a case where a powder-like fluoridation pitch is used, perviousness or impregnating ability to fine pores of a porous catalyst layer or the surface of a conductive granule can be improved further, and a more uniform and detailed three-phase zone can be formed. Therefore, while being able to continue further at a long period of time, being able to maintain a three-phase-circuit interface stably and being able to extend the life-span of [ a

catalyst bed ], a contact rate of a three phase ingredient can be raised.

[0036]As a solvent which dissolves or distributes said solid state fluoridation pitch, For example, monochlorotrifluoromethane, dichloro difluoroethane, Monochlorodifluoromethane, trichlorofluoroethane, dichlorotetrafluoroethane, Monochloropentafluoroethane, hexafluoro benzene, and perfluoro alkanes. Various kinds of fluorine system solvents, such as a liquefied fluoridation pitch currently indicated by low polymer of fluoride content monomers, such as various fluorine system compounds, such as perfluoro alkylamine, and chlorotrifluoroethylene, and JP,2-271907,A, are mentioned. these solvents -- a kind -- or two or more sorts may be used.

[0037]As mentioned above, since perviousness is high while a fluoridation pitch shows high water repellence compared with the conventional fluoro-resin, even if it is little, big water repellence can be given. therefore -- the amount of fluoridation pitch used can be chosen in the wide range according to a using form of a fluoridation pitch, directions for use, etc. -- for example, 0.1- of the whole constituent -- it is about 2 to 30 % of the weight still more preferably one to 40% of the weight preferably 50% of the weight.

[0038]In order that an electrode catalyst constituent may give water repellence to a catalyst bed and may secure gas permeation nature and diffusibility, it is preferred that powder-like bending resin which has water repellence is included. To bending resin which has water repellence, a fluoro-resin, for example, polytetrafluoroethylene, A tetrafluoroethylene hexafluoropropylene copolymer, an ethylene-tetrafluoroethylene copolymer, A tetrafluoroethylene perfluoroalkyl vinyl ether copolymer, An ethylene-chlorotrifluoroethylene copolymer, a tetrafluoroethylene hexafluoropropylene perfluoroalkyl vinyl ether copolymer, polyvinylidene fluoride, etc. are contained.

[0039]Resin of not less than 250 \*\* with heat resistance high to a desirable fluoro-resin, for example, the melting point, An about 260-350 \*\* fluoro-resin, for example, polytetrafluoroethylene, a tetrafluoroethylene hexafluoropropylene copolymer, and a tetrafluoroethylene perfluoroalkyl vinyl ether copolymer are contained preferably. Especially a desirable fluoro-resin is polytetrafluoroethylene.

[0040]Bending resin which has water repellence is usually used by the shape of a powder. Particle diameter of powder-like bending resin is about 0.1-30 micrometers, and can also be used as dispersing elements, such as an emulsion, for example.

[0041]Content of binding resin which has water repellence is suitably chosen in the range which can form a porosity channel in a catalyst bed, and can give water repellence, for example, is about 20 to 40 % of the weight still more preferably ten to 50% of the weight preferably five to 60% of the weight to the whole constituent.

[0042]Conductive carbon powder grain which supports catalyst components, such as a platinum group catalyst component, in a desirable electrode catalyst constituent of this invention. (For example, conductive carbon black) 5 to 60 % of the weight of powder-like bending resin (for example, powder-like polytetrafluoroethylene) which has water repellence, and a constituent



which contains 1 to 40 % of the weight of fluoridation pitches of not less than 120 degrees of angles of contact over water in 30 \*\* are contained ten to 80% of the weight.

[0043]In a constituent of this invention, a catalyst component and conductive carbon powder grain may be processed with a fluoridation pitch with powder-like bending resin using various methods, such as spreading, being impregnated, heating, and vacuum evaporation, if needed.

[0044]A catalyst composition may contain in an electrode reaction conductive fibers, such as various inertness additive agents, for example, a bulking agent, carbon fiber, and an activated carbon fiber, textiles (for example, polytetrafluoroethylene fiber etc.) which have water repellence, etc.

[0045]When an electrode catalyst constituent of this invention obtains an electrode material which continued at a long period of time and could maintain a three-phase zone in a catalyst bed and with which high water repellence was given, it is useful. An electrode material is obtained by forming a catalyst bed in a conductive base material using said constituent. In a fuel cell, an electrode material is gas diffusion electrode material which has gas permeation nature by porosity in many cases.

[0046]As opposed to optical anisotropy porous carbon minute granular-active-carbon 100 weight section obtained by carrying out activation of various porosity conductive base materials which have gas permeation nature and conductivity, for example, the meso carbon micro beads, to said conductive base material, 20 to binding material 500 weight section in which carbonization of phenol resin etc. or graphitization is possible, And zero to carbon fiber or textiles in which carbon fibrosis is possible 500 weight section is mixed, A substrate obtained by carbonizing or graphitizing after carrying out compression molding (JP,5-166513,A), 15 to 50 % of the weight of binding materials of 40 to 75 % of the weight of carbonization yields of 20 to 50 % of the weight of staple fibers of carbon fiber or textiles in which carbon fibrosis is possible, phenol resin, etc., And a substrate (JP,5-205750,A) etc. which are obtained by carbonizing or graphitizing a carbonaceous preforming object of paper-making structure which contains 30 to 60 % of the weight of organic particulate matters (pore formation agent) of 30 or less % of the weight of carbonization yields among thermosetting resin or thermoplastics are contained.

[0047]A conductive base material, for example as indicated by JP,5-325984,A, 10 to 60 % of the weight of binding materials of 40 to 85 % of the weight of carbonization yields of 10 to 60 % of the weight of staple fibers of carbon fiber or textiles in which carbon fibrosis is possible, phenol resin, etc., It may be a substrate obtained by carbonizing or graphitizing 15 to 60 % of the weight of organic particulate matters (pore formation agent) of 30 or less % of the weight of carbonization yields, and a carbonaceous preforming object of paper-making structure containing 10 to 30 % of the weight of fibrous binders among thermosetting resin or thermoplastics.

[0048]In order that a conductive base material may improve thermal conductivity, textiles [ in which carbon fibrosis is possible ], and/or carbon fiber 100 weight section is received, It may be a substrate obtained by carbonizing or graphitizing a preforming object of paper-making structure

containing 20 to binding material 250 weight section in which carbonization of 40 to 75 % of the weight of carbonization yields or graphitization is possible, and ten to pitch 250 weight section. As said pitch, an isotropic pitch and an anisotropy pitch which have about 150-400 \*\* softening temperature can be used. Said preforming object may contain ten to organic particulate matter 500 weight section which consists of a hardened material of an organic particulate matter (pore formation agent), for example, an organic particulate matter which consists of a hardened material of thermosetting resin, and thermosetting resin containing a pitch to textiles 100 weight section. Gas permeation nature etc. may be improved by using textiles in which carbon fibrosis is possible.

[0049]In a desirable conductive base material, gas permeability ( $\text{ml-mm/hr-cm}^2$  and  $\text{Aq}$ ), for example 850 (1500 to about [ Preferably 1000-4000, still more preferably ] 3500) or more. 2.0 or more (3.0 to about [ Preferably ] 10.0) porous carbon materials are contained for thermal conductivity ( $\text{kcal/m-hr-cm}^2$ ) of a thickness direction. Flexural strength ( $\text{kg/cm}^2$ ) of this porous carbon material may be 130 (150 to about [ Preferably ] 400) or more, and compressive strength ( $\text{kg/cm}^2$ ) may be 50 (50 to about [ Preferably ] 200) or more.

[0050]A catalyst bed formed in one field of said conductive base material can be formed by various methods. For example, when the \*\* aforementioned constituents are a fluid constituent containing a solvent and which can be applied, for example, dispersion liquid, a slurry, a paste, etc., a conductive base material is applied by a conventional method, for example, methods, such as coating and dipping, and a catalyst bed can be formed by drying. After applying said constituent to films and sheets, such as polyethylene terephthalate, a catalyst bed may be formed by transferring to one field of a conductive base material.

[0051]After forming in one field of \*\* conductive base material a layer containing powder-like bending resin which has a catalyst component, a conductive granule (conductive carbon powder grain with which a catalyst component was supported especially), and water repellence, a catalyst bed can be formed also by processing in a fluoridation pitch. On the occasion of processing by a fluoridation pitch, it uses that a fluoridation pitch is solvent fusibility, Using a solvent solution or dispersion liquid of a fluoridation pitch, said layer may be processed, and it may dry by methods, such as spraying, spreading, and immersion, it may replace with disposal methods, such as said spraying, using a fluoridation pitch having vacuum evaporation nature, and deposition treatment of the fluoridation pitch may be carried out to said layer. Fine pores of a catalyst bed, etc. may be made to permeate or diffuse a fluoridation pitch by heating a layer containing a fluoridation pitch using a fluoridation pitch having softening temperature or the melting point. A method of using a solution of a fluoridation pitch has the advantage that uniform processing can be performed simple.

[0052]Processing by a fluoridation pitch may be performed after forming and heat-treating a layer containing powder-like bending resin which has a catalyst component, a conductive granule, and

water repellence. temperature which powder-like bending resin which has water repellence welds heat treatment, and can form a gas permeation nature porous catalyst layer -- for example, not less than 200 °C can be preferably performed at about 250-400 °C.

[0053]\*\* catalyst bed may not be based on above methods, but may be formed by laminating a sheet obtained with powder-like bending resin which has water repellence if needed by fabricating a catalyst component, a conductive granule, and a fluoridation pitch to a sheet shaped to one field of a conductive base material.

[0054]Since a layer containing a fluoridation pitch carries out osmosis diffusion of the fluoridation pitch uniformly on fine pores of a catalyst bed, or the surface of a conductive granule, it is heat-treated by calcination etc. in many cases. In using powder-like bending resin which has water repellence as an ingredient which constitutes a catalyst bed, in order to bind powder-like bending resin and to form much fine pores in a catalyst bed, heat-treating by calcination etc. is preferred. Heat treatment temperature can be chosen according to the fluoridation softening point of pitch, the melting point, and softening temperature and the melting point of powder-like bending resin, for example, is about 250-380 °C still more preferably 250-400 °C preferably not less than 200 °C. A fluoridation pitch carries out osmosis diffusion uniformly on fine pores of a catalyst bed, or the surface of a conductive granule, and a catalyst bed in which a three-phase zone was formed with sufficient accuracy is formed by such heat treatment. If a layer containing bending resin is heat-treated by heating calcination etc., powder-like binding resin joins mutually, makes it function as a binder, and can unify a catalyst bed. Heat treatment is performed under an inert gas atmosphere of nitrogen, helium, argon, etc., or a vacuum.

[0055]Said catalyst bed may be formed in a field by the side of electrolysis solutions, such as phosphoric acid, in a fuel cell among conductive base materials. Gas passageways, such as a groove for supplying fuel to the electrolysis solution side through fine pores of a conductive base material, may be formed in a field of a catalyst bed and an opposite hand among said conductive base materials.

[0056]In a desirable electrode material, in one field of a porosity conductive base material. \*\* Conductive carbon powder grain which supports a platinum group catalyst component (for example, conductive carbon black), Powder-like bending resin which has water repellence (for example, powder-like polytetrafluoroethylene), And a catalyst bed by which a catalyst bed which comprised a fluoridation pitch of not less than 110 degrees of angles of contact over water in 30 °C, conductive carbon powder grain which supports \*\* platinum group catalyst component, and powder-like bending resin which has water repellence were processed with a fluoridation pitch is formed.

[0057]In a catalyst bed of an electrode material, a fluoridation pitch is permeated or diffused in detailed fine pores and a cavity part of a porous catalyst layer with disposal methods, such as being impregnated and heat melting. Therefore, a three-phase zone can be formed also in fine pores and a cavity part which were not yet used effectively, area of a three-phase zone is

increased, and contacting efficiency of a three phase ingredient can be raised using a homogeneous and detailed three-phase zone.

[0058]In these catalyst beds, rates of each ingredient are 10 to 80 % of the weight of conductive carbon powder grain which supports catalyst components, such as a platinum group catalyst component, 5 to 60 % of the weight of powder-like bending resin which has water repellence, and about 1 to 40 % of the weight of fluoridation pitches.

[0059]An electrode material of this invention can be used as the negative pole and the anodes, such as various electrodes of a fuel cell, for example, a hydrogen-oxygen fuel cell, and a methanol air fuel cell. In a fuel cell, various electrolysis solutions, such as phosphoric acid, can be used and an electrolysis solution may be not only a drainage system but a non-drainage system.

[0060]

[Effect of the Invention]Since it contains the fluoridation pitch, the electrode catalyst constituent of this invention controls a water-repellent fall, continues at a long period of time, and can maintain the three-phase zone in a catalyst bed stably. The life-span of [ the catalyst bed in a fuel cell ] can be extended. Therefore, it is useful, when covering a long time and operating a fuel cell stably at high efficiency.

[0061]Since it is provided with the catalyst bed which has the outstanding characteristic like the above, when the electrode material of this invention covers a long time and operates a fuel cell stably, it is useful.

[0062]According to the method of this invention, the electrode material provided with the catalyst bed which has the outstanding characteristic like the above can be manufactured by a simple method.

[0063]

[Example]Below, based on an example, this invention is explained more at details.

[0064]After adding double the amount of hydrogenation anthracene oil to the coal tar pitch of 100 \*\* of preparation softening temperatures of a fluoridation pitch (1), 0.2 % of the weight of quinoline insoluble, and 30 % of the weight of benzene insolubles and heating for 90 minutes at 430 \*\*, under decompression, hydrogenation anthracene oil was removed at 300 \*\*, and the reduction pitch was obtained. Nitrogen gas was introduced into the obtained reduction pitch, the low molecular weight constituent was removed, thermal polymerization was carried out at 400 \*\* for 5 hours, and the mesophase pitch of 300 \*\* of softening temperatures, 60 % of the weight of quinolines insoluble, 98 % of the weight of benzene insolubles, and 90 % of the weight or more of mesophase content was obtained.

[0065]The obtained pitch of 50 g was taught to the reaction vessel made from nickel, evacuation of the inside of a system was carried out, and it filled with argon gas. Subsequently, when 20% of fluoride and argon 80% of mixed gas was circulated the speed for 70 \*\* and 650 cc of mean velocity/and was made to react for 20 hours, the fluoridation pitch of 144 g was obtained. The angle of contact over water [ in / the empirical formula of a fluoridation pitch is CF1.38 as a result

of ultimate analysis, and / softening temperature =260 °C and number average molecular weight = about 3300 and 30 °C ] = it was 145 degrees. The angle of contact was measured by the sessile drop method using the FACE angle-of-contact meter (Harmony Interface Science nature, CA-A type).

[0066]After heat-treating the obtained fluoridation pitch by 250 °C and 10torr for 10 hours, it ground and the fluoridation pitch particle (henceforth a fluoridation pitch (1)) with a mean particle diameter of 1.3 micrometers was obtained.

[0067]replacing with the preparation above-mentioned mesophase pitch of a fluoridation pitch (2) - a pitch (the Mitsubishi Gas Chemical Co., Inc. make.) The fluoridation pitch of 143 g was obtained like the method of preparation of the above-mentioned fluoridation pitch (1) except using pitch ARA24, 290 °C of softening temperatures, 98.4 % of the weight of hexane insoluble elements, and 50 g of pyridine 45.7-% of the weight insoluble elements. The angle of contact over water [ in / the empirical formula of a fluoridation pitch is CF1.33 as a result of ultimate analysis, and / softening temperature =250 °C and number average molecular weight = about 3100 and 30 °C ] = it was 145 degrees.

[0068]After heat-treating the obtained fluoridation pitch by 250 °C and 10torr for 10 hours, it ground and the fluoridation pitch particle (henceforth a fluoridation pitch (2)) with a mean particle diameter of 1.3 micrometers was obtained.

[0069]The slurry of the platinum support acetylene black which supported 10% of the weight of the platinum catalyst to acetylene black was prepared by mixing an acetylene black ultrafine particle (particle diameter of 0.1-0.3 micrometer, mean particle diameter of 0.2 micrometer), and returning into Example 1 - 4 chloroplatinic acid solutions. The slurry of platinum catalyst support acetylene black, a fluoridation pitch (1), a fluoridation pitch (2), and the dispersion liquid containing polytetrafluoroethylene (PTFE) were mixed, and the paste of the rate shown in a table was prepared by solid content conversion.

[0070]And the obtained paste was calcinated at 290 °C under an inert gas atmosphere for 2 hours, after using and applying the spatula to the nature substrate of porous carbon (10 cm x 10 cm, and 1.2 mm in thickness) and drying at 100 °C for 3 hours, and the electrode material was produced.

The quantity of the platinum catalyst in each electrode material is 0.5mg/[cm]<sup>2</sup>.

[0071]Example 5 - 8 cathode catalyst (N.E. Chemcat make, PC10FA) 50 weight section, polytetrafluoroethylene (PTFE) 25 weight section, or 40 weight sections are kneaded and rolled, The 0.3-mm-thick catalyst sheet was produced by preparing the sheet for electrodes and calcinating for 30 minutes at 350 °C under an inert gas atmosphere.

[0072]After impregnating the obtained catalyst sheet with the hexafluoro benzene solution of a fluoridation pitch (1) and a fluoridation pitch (2), respectively, hexafluoro benzene was removed to it and it processed in the fluoridation pitch to it. It impregnated with each fluoridation pitch at a rate which is solid content conversion and is shown in a table. The catalyst sheet impregnated with fluoridation PITSUCHI (1) was 300 °C, and the catalyst sheet impregnated with the fluoridation

pitch (2) is 275 \*\*, and was calcinated under an inert gas atmosphere, respectively.

[0073]And the electrode material was produced by pasting up each catalyst sheet processed in the fluoridation pitch on the nature substrate of porous carbon (100 mm x 100 mm, and 1.2 mm in thickness). The quantity of the platinum catalyst in each electrode material is  $0.5\text{mg}/\text{cm}^2$ .

[0074]The electrode material was produced like Examples 1-4 except mixing the slurry of platinum catalyst support acetylene black, and the dispersion liquid containing polytetrafluoroethylene (PTFE) at a rate shown in a table, without using the comparative example 1 - 3 fluoridation pitch.

[0075]The electrode material was produced like Examples 5-8 except using a cathode catalyst and polytetrafluoroethylene (PTFE) at a rate shown in a table, without using a comparative example 4 fluoridation pitch.

[0076]And the cathode single electrode was produced using the electrode material obtained by Examples 1-8 and the comparative examples 1-4, a platinum mesh was made into the counter electrode, the measuring device shown in drawing 1 using 105% phosphoric acid as an electrolysis solution was equipped, and the battery characteristic was measured at 200 \*\*.

[0077]This device is provided with the tub 1 which accommodates the phosphoric acid 2 as an electrolysis solution, and the holder 3 formed in this tub 1. While this holder 3 is provided with the cap 6 for attaching the cathode 5 for equipping the hollow cylinder-like case 4 and case opening side, and this cathode, the air supply port 7 and the air exhaust port 8 for supplying air to said cathode 5 are provided in said case 4.

[0078]In said tub 1, the hydrogen reference electrode 9 which comprised a RUGIN capillary tube provided with the platinum stick 10 is also formed, and hydrogen gas is supplied to this hydrogen reference electrode 9 from the hydrogen supply line 11. The voltmeter 12 is connected between said cathode 6 and the platinum stick 10 of the hydrogen reference electrode 9. The platinum mesh as the counter electrode 13 is immersed in said phosphoric acid liquid 2, and the current source 14 for carrying out load of the over-current to said cathode 6 is connected to it between this counter electrode 13 and said cathode 6.

[0079]Hydrogen gas was supplied and air was supplied by a part for speed-of-supply/of 100 ml by speed-of-supply/of 30 ml when measuring. Cathode electromotive force (IR-free vs.RHE) when the current of  $200\text{ mA}/\text{cm}^2$  was impressed was measured, and it was considered as the initial characteristic. When measuring a battery characteristic, the accelerated test which gives an overload to an electrode estimated the endurance of the electrode. Namely, you apply current density for 1 minute from  $200\text{ mA}/\text{cm}^2$ , only  $100\text{ mA}/\text{cm}^2$  makes it increase, and it holds for 1 minute, Subsequently, the operation which is applied for 1 more minute, and only  $100\text{ mA}/\text{cm}^2$  makes increase, and is held for 1 minute, After carrying out gradually until current density became  $1000\text{ mA}/\text{cm}^2$ , the cycle in which current density is gradually reduced for every  $100\text{ mA}/\text{cm}^2$  to  $200\text{ mA}/\text{cm}^2$  contrary to the above was repeated, and the change of potential for every cycle was observed.

[0080]The initial characteristic (initial voltage) of Example 1 was 850 mV, set this value to 100 and evaluated the generated voltage relatively. A result is shown in a table. Among front, a catalyst bed begins to drop out in phosphoric acid liquid, polarization becomes very large, and "-" shows that it was incapable measurement.

[0081]

[Table 1]

表

	触媒層の組成 (重量%)			発生電圧 (相対値)			
	触媒担持導電性 粉 粒 体	P T F E	フッ化ピッチの 種 類 と 量	初 期 特 性	1 サイクル	2 サイクル	3 サイクル
実施例 1	62. 5	31. 25	(1) 6. 25	100	100. 7	99. 9	99. 9
実施例 2	62. 5	31. 25	(2) 6. 25	100. 3	100. 1	100. 1	100. 2
実施例 3	50. 0	25. 0	(1) 25. 0	91. 9	99. 5	99. 5	99. 5
実施例 4	50. 0	25. 0	(2) 25. 0	98. 8	100. 3	100. 1	99. 7
比較例 1	50. 0	50. 0	—	99. 9	99. 2	98. 4	97. 2
比較例 2	62. 5	37. 5	—	101. 3	100. 0	98. 7	97. 0
比較例 3	66. 7	33. 3	—	102. 1	100. 8	99. 7	98. 2
実施例 5	50. 0	25. 0	(1) 25. 0	91. 2	96. 9	99. 2	102. 0
実施例 6	50. 0	25. 0	(2) 25. 0	88. 3	96. 8	99. 2	101. 5
実施例 7	50. 0	40. 0	(1) 10. 0	86. 9	97. 1	98. 9	98. 9
実施例 8	50. 0	40. 0	(2) 10. 0	93. 1	98. 7	100. 7	99. 3
比較例 4	50. 0	50. 0	—	100. 3	99. 2	97. 9	96. 1

From a table so that clearly in the electrode material of an example, Although a slightly low electrode material has initial voltage, even if the electrode material of an example repeats the cycle which gives an overload compared with the electrode material of a comparative example, it does not have the fall of voltage, and it generates conversely high voltage in many cases, and its endurance of a catalyst bed is improving greatly. Since the voltage characteristic falls one by one for every cycle, the electrode material of a comparative example has the small endurance of a catalyst bed, and cannot bear prolonged operation.

[Translation done.]